



Synthesis of covalent organic polymers for removing CO₂ and heavy metal ions with strong affinity

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Conference Proceeding

(Preliminary Version, Final Version will be edited after the meeting*)

*N.B. – Authors are invited to signal corrections in the mean time to improve this draft.

제8회 유럽한국과학기술대회 Eighth Euro-Korean Conference on Science and Technology

Faculté de Médecine, Strasbourg, France, 22-24 July 2015



Engineering and Technology

Location: Room 209 (Building "Forum")

Date & Time: 2015-07-24 14:00-16:00

Session Chair: Prof. PARK, Chung Hae

14:00 - 14:20
<p>Dr. LEE, Eungjang CELIA, University of Bordeaux</p> <p><i>Aberration Corrected Direct Laser Writing on Silver-containing Phosphate Glass</i></p>
14:20 - 14:40
<p>Mr. KIM, Sangyeob Department of Environmental Engineering and Water Technology, UNESCO-IHE Institute</p> <p><i>Applicability of high pressure supersaturating oxygenation to MBRs wastewater treatment</i></p>
14:40 - 15:00
<p>Ms. JANG, Jiyi KIST-Europe</p> <p><i>Computational approaches for predicting toxicity of chemical mixtures</i></p>
15:00 - 15:20
<p>Dr. KWAK, Sanghoon Verimag, University of Joseph Fourier</p> <p><i>DESIGN OF ASYNCHRONOUS MSP430 MICROPROCESSOR</i></p>
15:20 - 15:40
<p>Mr. OH, Hyondong Department of Aeronautical and Automotive Engineering, Loughborough University</p> <p><i>Coordinated Standoff Tracking of Moving Ground Targets Using Unmanned Aerial Vehicles for Airborne Persistent Surveillance</i></p>
15:40 - 16:00
<p>Mr. KIM, Yong-Ki Chungbuk National University</p> <p><i>Recognition of Isolated Words Represented by Lip Image Streams using Dynamic Time Warping</i></p>

Poster Presentation

Dongah Ko

Department of Environmental Engineering, Technical University of Denmark

Synthesis of covalent organic polymers for removing CO₂ and heavy metal ions with strong affinity

Jihye Hwang

Department of chemical engineering, Norwegian University of Science and Technology

Optimization of absorber column

Eomji Park

Mechanical Engineering, Technische Universität Wien

Design Home-security robot based on OPRoS

Won Jong KIM

Department of Information Display and Advanced Display Research Center, Kyung Hee University

Cathodoluminescence Properties of Silicon Thin Films with Carbon Nanotube Electron Beam (C-beam) Exposure Technique

Minji Park

Environmental Safety Group, KIST Europe

EU CLP vs Korea GHS for Chemical Mixtures: A Solution for Korean Chemical Industry

Bongwoo Kwak

Automotive Components & Materials R&D Group, KITECH

Design of Wireless Power Transfer System with Hybrid of Inductive Coupling and Magnetic Resonance for Charging Electric Vehicle

Youngkuk Choi

Automotive Components & Materials R&D Group, KITECH

Design of Operational Drive System of Agricultural Unmanned Transportations

Jong Gwan Lim received the MS degree in biosystem engineering at KAIST (2006). He is a currently Ph.D candidate at the same university. His current research interests include Human-Robot Interaction (HRI), Machine Learning and Pattern Recognition.

Mi-Hye Kim received the Ph. D degree in mathematics from Chungbuk National University, (2001) She is currently a professor of department of computer engineering in the same university. Her research interests are mainly in the field of fuzzy theory & application, ubiquitous game and gesture recognition.

Synthesis of covalent organic polymers for removing CO₂ and heavy metal ions with strong affinity

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Abstract

Demand for functionalized adsorbent that contains not only high surface area but also selectivity and recyclability has been increased for several decades. Especially, growing environmental problems such as water pollution by heavy metal ions and global warming due to carbon dioxide concentration introduced various application possibilities of functionalized adsorbents for pollutant treatment. Since both carbon dioxide and heavy metal ions are non-degradable and stable compounds, those are difficult to be removed from polluted sites. Therefore, adsorption mechanism considered as a promise solution for removing those pollutants. Conventional technologies for both heavy metal ions and CO₂ treatment systems have encountered a number of limitations. In case of CO₂ treatment system, monoethanolamine (MEA) has been used for more than 60 years because of their low-cost with rapid reaction, however, insufficient CO₂ loading capacity and easy degradation of materials are still remained as a barrier [1]. Also, in the case of heavy metal ions treatment, activated carbon (AC) is commonly used for treatment due to its high porosity and low-cost, it has no functionality to uptake targeted pollutant selectively from heterogeneous circumstance. Besides, both MEA and AC regeneration process consumes considerable amount of energy, hence, used materials tend to be incinerated or thrown out rather than regenerated. Likewise, fulfilling only some conditions and ignoring others will lower the whole process efficiency during the treatment. Recently, porous polymers with various functionalities are suggested as a replacement of conventional methods to overcome several constrains. In this study, we designed functionalized covalent organic polymers (COPs) and synthesized it by bottom up methods to generate specific functionalities. By introducing functionalities into COPs we could enhance selectivity of adsorbent towards treatment target substances with sufficient surface area and porosity of adsorbent [2,3]. Surface area and porosity of functionalized COPs are analysed by Brunauer-Emmett-Teller (BET) surface area

method and scanning electron microscope (SEM) and functionalities are confirmed by elemental analysis (EA), Fourier transform infrared (IR), and Thermo-gravimetric analysis (TGA). CO₂ capacity, selectivity, isosteric heat of CO₂ adsorption was measured and calculated by BET, Ideal Adsorbed Solution Theory (IAST) equation and Van't Hoff equation. Lastly, heavy metal removal amount, isotherm, and kinetic were measured by Inductive coupled plasma mass spectrometry (ICP-MS) and Atomic adsorption spectroscopy (AAS). Here, we present functionalized COPs, one for CO₂ adsorption that achieved sufficient CO₂ capacity with 61 of CO₂-N₂ selectivity owing to a nitrogen-rich structure and other for heavy metal ion treatment which carried sulfur functionality and achieved high selectivity towards heavy metals ions. All COPs showed thermal stability and low heat of adsorption which facilitating easy regeneration.

Keywords: *Covalent organic polymer, Functionalized adsorbent, Carbon dioxide capture, Heavy metal ions, Environment*

References

- [1] Mohammad Songolzadeh, Mansooreh Soleimani, Maryam Takht Ravanchi, and Reza Songolzadeh, Carbon dioxide separation from flue gases: a technological review emphasizing reduction in greenhouse gas emissions, *The Scientific World Journal*, 2014, vol. 2014, 34
- [2] Dongah Ko, Hasmukh A. Patel, Cafer T. Yavuz, 2015, Synthesis of Nanoporous 1,2,4-oxadiazole networks with high CO₂ capture capacity, *Chem. Commun.*, 51, 2915-2917.
- [3] Hasmukh A. Patel, Dongah Ko, Cafer T. Yavuz 2014, Nanoporous Benzoxazole Networks by Silylated Monomers, Their Exceptional Thermal Stability, and Carbon Dioxide Capture Capacity, *Chem. Mater.*, 26 (23), pp 6729–6733.

Biography

Dongah Ko is PhD student in Technical University of Denmark. She finished her B.S degree in Environmental science department from Kyung Hee University. She received her Master's degree at the Graduate School of Energy, Environment, Water and Sustainability (EEWS), Korea Advanced Institute of Science and Technology (KAIST) under supervision of Dr. Cafer T. Yavuz. In KAIST her research was focused on development of new covalent organic polymers for carbon dioxide capture. Currently, with same covalent organic polymers, she is working on heavy metal ion removal from polluted water under supervision of Dr. Henrik R. Andersen and Dr. Cafer T. Yavuz.

Optimization of absorber column

Jihye Hwang

Department of chemical engineering, Norwegian University of Science and Technology, Trondheim, Norway (jihye9996@gmail.com)

Abstract

Carbon dioxide is an important factor related to greenhouse gases and has a significant contribution to global warming. Therefore the importance of researching, optimizing and developing the concept of CO₂ capture from flue has increased. To date, it exist three main approaches to capture CO₂ generated from a primary fossil fuel (coal, natural gas or oil), biomass, or mixture of these fuels, and these are as follows; post-combustion, pre-

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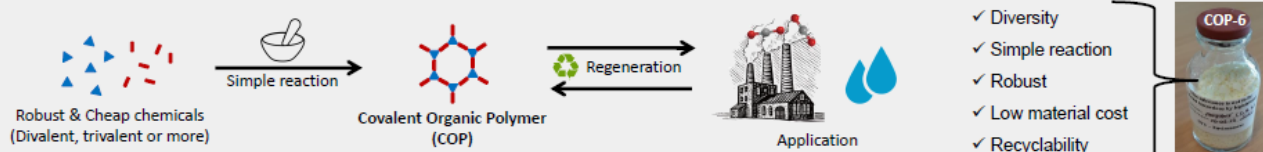
¹ Technical University of Denmark, Department of Environmental Engineering, Miljøvej 113, 2800 Lyngby, ² Technical University of Denmark, Department of Micro- and Nanotechnology, Ørstedss Plads, Bygning 345B, 2800 Kgs. Lyngby, ³ Korea Advanced Institute of Science and Technology (KAIST), Graduate School of EEWs, Daejeon 305-701, Republic of Korea



doko@env.dtu.dk

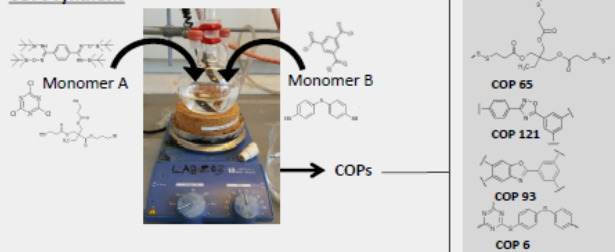
The demand for functionalized adsorbent that contains not only high surface area but also selectivity and recyclability has increased for several decades. Especially, growing environmental problems such as water pollution and global warming introduced various application possibilities of functionalized adsorbents for pollutant treatment. Our target contaminants are CO₂ and heavy metal ions and they are non-degradable, stable compounds. Hence, adsorption mechanism is considered as a promising solution for removing those pollutants. In this study, we developed several kinds of Covalent Organic Polymers (COPs) and applied them as a functionalized adsorbent for pollutant treatment systems.

1. Covalent Organic Polymers (COPs)



2. Experimental methods

COPs synthesis



Heavy metal ions removal

- Atomic Absorption Spectroscopy
- Sampling time: 10 min, 1 h, 3 h, 24 h, 48 h
- pH measure: Initial point, final point
- BET instrument: volumetric type measurement
- Measurement conditions: ~ 1 bar, 273 K, 298 K
- Selectivity (N₂/CO₂): Ideal Adsorption Solution Theory (IAST) calculation

CO₂ capture

3. Result and Discussion - CO₂ capture

	MEA ^[1]	COP 121		COP 93		
	298K	273K	298K	273K	298K	323K
BET surface area	solution	24.5 m ² g ⁻¹		605.8 m ² g ⁻¹		
CO ₂ uptake (mg g ⁻¹)	60	87.1	59.4	139.6	91.1	60.7
N ₂ uptake (mg g ⁻¹)	NA	5.1	7.5	6.8	4.4	2.3
Selectivity ^[2]	NA	62	29	75.1	73.5	99.2
Thermal stability	110-130°C	up to 450°C		up to 550°C		

[1] Monoethanolamine

[2] Selectivity calculated by IAST calculation

✓ In order to fill up 500 ml bottle with CO₂, 11 g of COP121 or only 7 g of COP 93 are needed.

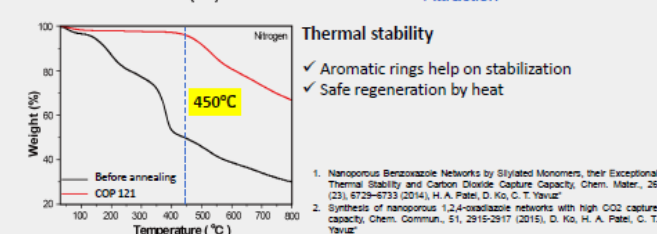
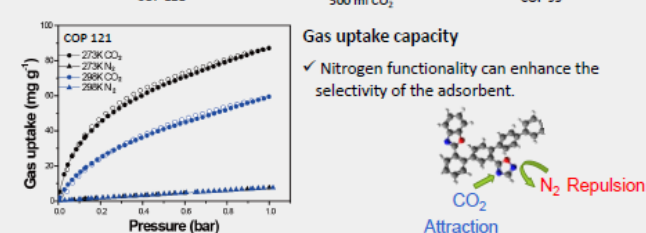
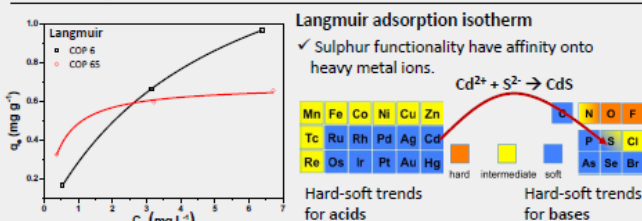


4. Results and Discussion - Heavy metal ion removal

	COP 6 ^[2]			COP 65 ^[2]		
Cd ²⁺ Initial concentration	0.7 ppm	4 ppm	7 ppm	0.7 ppm	4 ppm	7 ppm
BET surface area	7.300 m ² g ⁻¹			0.001 m ² g ⁻¹		
% removal ^[1] of Cd ²⁺	24%	18%	13%	48%	16%	9%
Langmuir maximum adsorption capacity	1.706 mg/g			0.695 mg/g		
R ²	0.9999			0.9995		

[1] % removal = $\frac{[C]_0 - [C]_e}{[C]_0} \times 100$ C₀ = initial concentration, C_e = equilibrium concentration

[2] Dose amount: 1g/L



5. Summary

